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# The Role of Grain Surface Reactions in the Chemistry of Star Forming Regions

Final Technical Report

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The importance of reactions at the surfaces of dust grains has long been recognized to be one of the two main chemical processes that form molecules in cold, dark interstellar clouds where simple, saturated (fully-hydrogenated) molecules such as  $H_2$ , water, methanol,  $H_2CO$ ,  $H_2S$ , ammonia and  $CH_4$  are present in quantities far too high to be consistent with their extremely low gas phase formation rates. In cold dark regions of interstellar space, dust grains provide a substrate onto which gas-phase species can accrete and react. Grains provide a "third body" or a sink for the energy released in the exothermic reactions that form chemical bonds. In essence, the surfaces of dust grains open up alternative reaction pathways to form observed molecules whose abundances cannot be explained with gas-phase chemistry alone. This concept is taken one step further in this work: instead of merely acting as

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a substrate onto which radicals and molecules may physically adsorb, some grains may actively participate in the reaction itself, forming chemical bonds with the accreting species. Until recently, surface chemical reactions had not been thought to be important in warm circumstellar media because adspecies rapidly desorb from grains at very low temperatures; thus, the residence times of molecules and radicals on the surface of grains at all but the lowest temperatures are far too short to allow these reactions to occur. However, if the adspecies could adsorb more strongly, via a true chemical bond with surfaces of some dust grains, then grain surface reactions will play an important role in warm circumstellar regions as well.

In this work, the surface-catalyzed reaction  $\text{CO} + 3 \text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$  is studied in the context that it may be very effective at converting the inorganic molecule CO into the simplest organic compound, methane.  $\text{H}_2$  and CO are the most abundant molecules in space, and the reaction converting them to methane, while kinetically inhibited in the gas phase under most astrophysical conditions, is catalyzed by iron, an abundant constituent of interstellar dust. At temperatures between 600 and 1000 K, which occur in the outflows from red giants and near luminous young stars, this reaction readily proceeds in the presence of an iron catalyst.

Iron is one of the more abundant elements composing interstellar dust. Its abundance relative to hydrogen is almost that of silicon, and both of these heavy elements are primarily locked up in dust at all but the hottest regions of interstellar space. The composition of inorganic interstellar dust is not

well known although  $[\text{Mg}, \text{Fe}] \text{SiO}_3$ ,  $[\text{Mg}, \text{Fe}]_2 \text{SiO}_4$ , and  $\text{FeS}$  are all thought to be abundant constituents. Iron oxides and metallic iron are also possible candidates. All of these minerals are found to varying degrees in ancient meteorites as well as in interplanetary dust particles. Some IDPs are scarred by billions of years' worth of solar flare tracks indicating their very great age and presolar (interstellar) origin. These particles are the most ancient and pristine of all extraterrestrial materials studied in the laboratory; hence, they are the closest relatives to interstellar dust of which we have physical samples. Small iron inclusions ranging in diameter up to a micron or so have been isolated from IDPs, and some of these grains are coated with a carbonaceous residue, evidence of having served as a catalyst for the reaction converting  $\text{CO}$  to organics. This physical evidence strongly supports the notion that not only does a population of iron grains indeed exist, but also that chemical reactions involving the conversion of  $\text{CO}$  to organics has occurred on their surfaces at some point in their lifetimes.

In addition to the encouraging evidence of a small but ubiquitous metallic grain component to cosmic dust, iron is quite chemically and physically stable at the low pressures and higher temperatures typical of circumstellar regions. As an element, iron is special because strongly bound molecular species such as  $\text{CO}$  and  $\text{H}_2$  readily adsorb and dissociate on this metal, but the bonds between  $\text{Fe}$  and  $\text{H}$ ,  $\text{C}$  and  $\text{O}$  atoms are not so strong that they preclude reactions amongst these adsorbates to form new molecules. Sulfur, an electronegative element which is a common and troublesome poison of in-

dustrial catalysts, is highly abundant and will most likely preclude catalysis at temperatures below about 700 K as  $\text{H}_2\text{S}$  will react with metallic iron to form  $\text{FeS}$ . Thus, catalysis will be efficient only at temperatures above 700 K.

To accomplish the goals of this project, a non-empirical kinetic model for the catalyzed reaction converting CO to methane was developed to apply to astrophysical conditions. Although empirical equations describing the dependence of the methane formation rate as a function of partial pressures of  $\text{H}_2$  and CO are available in the literature, these equations assumed a rate-limiting step for this reaction and were thus unreliable for any temperature and pressure outside the range for which they were measured. Therefore, a model was required which took into consideration *all* of the steps in the reaction instead of first assuming which one was rate-limiting. A more accurate determination of the rates was achieved; in fact, the rate-limiting step for any pressure and temperature can be isolated in this way.

The rate of methane formation in the outflows from oxygen-rich red giants was shown to be sufficient to account for this pathway to be the source of the reactive form of carbon originating deep in the outflow. Since the temperatures in outflows drops rapidly, this conversion must occur over a fairly brief period of time, within about ten years. In these regions, it is this short period of time between grain condensation and  $\text{FeS}$  formation (which occurs once the outflow cools to below 700 K) which will limit the amount of CO which gets converted to methane. In most of this region, the rate-limiting step of the reaction is CO adsorption, due to the extremely low

partial pressures prevalent throughout the outflow. The surface area of iron grains is also an important factor as the amount of methane formed will scale proportionally to the relative abundance of catalyst sites. The mass loss rate is the outflow parameter which most significantly affects the results from the chemical model. High mass loss rates correspond to high densities, and thus high arrival rates of CO. The temperature power law ( $\alpha$ ), dust condensation temperature, and terminal outflow velocity do not factor as significantly into the conversion rate or the final CH<sub>4</sub>/CO ratio. I conclude that the amount of methane formed via catalysis on a relatively conservative amount of large metallic iron grains can account for the organics observed in the warm dusty envelopes around some oxygen-rich red giants.

The physical conditions of the remnant molecular cloud enshrouding young stellar objects are found to be conducive to catalyzed conversion of CO to methane, which would have an important impact in the evolution of organic material in regions of star formation. In the inner portions of the “catalysis zone,” the high temperatures keep the number of hydrogen atoms adsorbed to a grain rather low, resulting in a low rate of hydrogenation of the surface carbide. Thus, it is this step which limits the overall rate of reaction closer to the star. In the outer portion of the “catalysis zone,” temperatures are lower, hydrogen coverages are higher, and the rate of CO arrival to a grain limits the rate of reaction, which is proportional to the gas density there. In the catalysis zone, the timescale for destruction of methane by reaction with the H<sub>3</sub><sup>+</sup> ion is on the order of 10<sup>5</sup> to 10<sup>6</sup> years, longer than the expected

lifetime of a region such as the Orion Hot Core (a few  $\times 10^4$  years). However, the short timescales required to convert large amounts of CO to methane suggests that the amount of this molecule formed via catalysis near embedded young stars may be very large in the relatively small physical extent of the catalysis zone.

The most general conclusion drawn from this work is that grain surface reactions can markedly influence the chemistry in warm circumstellar media, and in particular, these processes can play a very important role in the chemical evolution of organic material in these regions. Thus, it is shown that grain surface reactions are efficient beyond the traditional confines of cold dark interstellar clouds.